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AB - J03090592 Mfg. surface treated cans used for producing cans by drawing and ironing (DI) comprises: continuously degreasing, Ni-plating, and continuously annealing; then refining rolling in dry state, opt. degreasing, and tin plating immediately after without pickling. Also claimed is process as above, which comprises refining rolling in wet state and degreasing, in place of refining rolling in dry state and opt. degreasing. Pref. the Ni plating is carried out by electroplating, to give Ni coverage of 0.01 - 0.5 g/m². Continuous annealing is conducted in reducing atmos. at 600 - 900 deg.C, for 10 - 90 s. Thin sheet of steel comprises, after annealing, Ni at concn. of 0.02 - 0.50 as expressed by Ni/(Fe+Ni) (wt. ratio), in surface Ni diffusion layer 10 - 5000 Angstrom thick.

- USE/ADVANTAGE - Provides at reduced process cost, surface treated sheet steel for DI cans with reduced amt. of Sn. (11pp Dwg.No.0/0)

IW - SURFACE TREAT SHEET STEEL MANUFACTURE DRAW IRONING CAN DEGREASE NICKEL PLATE CONTINUOUS ANNEAL REFINE ROLL DEGREASE TIN PLATE

IKW - SURFACE TREAT SHEET STEEL MANUFACTURE DRAW IRONING CAN DEGREASE NICKEL PLATE CONTINUOUS ANNEAL REFINE ROLL DEGREASE TIN PLATE

NC - 001

OPD - 1989-08-31

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PAW - (KAWI) KAWASAKI STEEL CORP

T - Surface treated sheet steel mfr. for drawing and ironing cans - by degreasing, nickel-plating, continuously annealing, refining rolling, degreasing and tin-plating, etc.

MACHINE-ASSISTED TRANSLATION (MAT):

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DI 缶用表面处理鋼板の製造方
法(54)[TITLE]
The manufacturing method of the surface-
treated steel sheet for DI can

(21) 【特願】

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【明細書】**[Specification]****【1. 発明の名称】**

DI 缶用表面処理鋼板の製造
方法

[1. TITLE]

The manufacturing method of the surface-treated steel sheet for DI can

【2. 特許請求の範囲】

(1) 薄鋼板を連続的に脱脂、ニッケルめっき、連続焼鈍し、ひきつづきドライ状態で調質圧延し、脱脂せずにまたは脱脂した後、酸洗を行わず直ちに錫めっきを行うことを特徴とする DI 缶用表面処理鋼板の製造方法。

(2) 薄鋼板を連続的に脱脂、ニッケルめっき、連続焼鈍し、ひきつづきウェット状態で調質圧延した後、脱脂を行い、酸洗を行わず直ちに錫めっきすることを特徴とする DI 缶用表面処理鋼板の製造方法。

(3) 前記ニッケルめっきが、ニッケルを電気めっきにて 0.01 ~ 0.5g/m² の付着量で鋼板表面に形成する請求項 1 または 2 に記載の DI 缶用表面処理鋼板の製造方法。

(4) 前記連続焼鈍が、還元性雰囲気中で、焼鈍温度 600 ~ 900°C、焼鈍時間 10 ~ 90 秒で行う請求項 1 ~ 3 のいずれかに記載の DI 缶用表面処理鋼板の製造方法。

[2. claim]

(1) Degrease continuously, and carry out nickel plating of the sheet steel, and it carries out a continuous annealing. After carrying out a temper rolling in the dry state continuously and not degreasing or degreasing, an acid wash is not performed but the tin plating is performed immediately.

The manufacturing method of the surface-treated steel sheet for DI can characterized by the above-mentioned.

(2) Continuously, degrease, and carry out nickel plating and carry out the continuous annealing of the sheet steel. After able to continue and carrying out a temper rolling in the state of a wet, it does not pickle by performing a degreasing and the tin plating is carried out immediately.

The manufacturing method of the surface-treated steel sheet for DI can characterized by the above-mentioned.

(3) The manufacturing method of the surface-treated steel sheet for DI can given in Claims 1 or 2 from which the above-mentioned nickel plating forms a nickel on the steel-plate surface in the amount of adhesion of 0.01 - 0.5 g/m² by the electroplating.

(4) The manufacturing method of one surface-treated steel sheet for DI can of Claim 1-3 which an above-mentioned continuous annealing performs in 600-900 degree C of annealing temperatures, and anneal time 10-90 seconds in a reducing atmosphere.

$$1\text{\AA} = 10^{-8}\text{cm} = 10^{-4}\mu\text{m}$$

JP 3-090592-A

DERWENT
★
THOMSON SCIENTIFIC

(5) 前記連続焼鈍後の薄鋼板が、表面 Ni 濃度 $\text{Ni}/(\text{Fe}+\text{Ni})$ (重量比) で 0.02~0.50、厚み 10~5000 Å のニッケル拡散層を形成する請求項 1~4 のいずれかに記載の DI 缶用表面処理鋼板の製造方法。

(6) 前記錫めっきが、錫を電気めっきにて 0.5~2.0 g/m² の付着量で鋼板表面に形成する請求項 1~5 のいずれかに記載の DI 缶用表面処理鋼板の製造方法。

(5) The manufacturing method of one surface-treated steel sheet for DI can of Claim 1-4 on which the sheet steel after an above-mentioned continuous annealing forms a nickel diffused layer with a thickness of 10-5000 angstroms by surface Ni concentration $\text{Ni}/(\text{Fe}+\text{Ni})$ (weight ratio) 0.02-0.50.

(6) The manufacturing method of one surface-treated steel sheet for DI can of Claim 1-5 from which the above-mentioned tin plating forms tin on the steel-plate surface in the amount of adhesion of 0.5 - 2.0 g/m² by the electroplating.

5000.
0.5um

【3. 発明の詳細な説明】

[3. DETAILED DESCRIPTION OF INVENTION]

【産業上の利用分野】

本発明は、電気めっきぶりきに絞りしごき加工を施して継ぎ目無し缶、即ち DI 缶 (Drawn and ironing) を製造するための DI 加工性と耐食性に優れた DI 缶用表面処理鋼板の製造方法に関する。

[INDUSTRIAL APPLICATION]

This invention relates to the manufacturing method of the surface-treated steel sheet for DI can excellent in DI workability and corrosion resistance for performing the dapple drawing and ironing to the electroplating tin plate, and manufacturing a jointless can (Drawn and ironing), i.e., DI can.

【従来の技術】

製缶用材料としてはぶりき、ティンフリー鋼板のごとき鉄系材料とアルミニウムの 2 種類がある。本発明の対象とする DI 缶にはぶりきとアルミニウムが現在使用されている。ぶりきは DI 加工後に、脱脂して、更にリン酸塩処理を施した後、内面 2 回塗装する。この塗装を 1 回にして缶コストを削減できれば、その経済的効果は極めて大きい。一方、現在 DI 缶用ぶりきとして使用されているのは、錫付着量 2.8 g/m² (片面当り) であるが、これを 1.8 g/m² ある

[PRIOR ART]

As a canning material, there are 2 kinds, the iron-type material like a tin plate and a tin free steel sheet, and an aluminium.

The tin plate and the aluminium are currently used for DI can made objective of this invention.

A tin plate is coated two inner surface, after degreasing and performing a phosphate process further after DI process.

If this coating is carried out once and can cost can be reduced, the economical effect is very large.

On the one hand, amount of tin adhesion 2.8 g/m² (per one side) is currently used as a tin plate for DI can.

However, request that this is decreased to 1.8 g/m²s or 1.0 g/m²s (per one side), and it will make a cheaper material is also strong.

いは 1. 0g/m² (片面当り) ま
で少なくしてより安価な材料に
しようという要求も強い。

通常半田缶、溶接缶などの缶
胴に使用されるぶりきは錫めっ
き後リフローにより Fe-Sn 合
金層を形成し、さらに何らかの
クロメート処理を施して作られ
る。それに対して、DI 缶用ぶり
きは、Fe-Sn 合金層があると
DI 加工用の金型の寿命を短く
なるためリフロー処理を施さな
いのが普通である。また、同じ
く金型の寿命の関係から、表面
のクロメート量を少なく制限す
る対策も特開昭 54-100944 号
で公知である。こうした、技術
は DI 缶用ぶりきを普及させる
のに効果はあったが、耐食性を
半ば犠牲にしたものであった。

【発明が解決しようとする課
題】

ぶりきを DI 加工する時、特に
しごき加工時に金属錫が無くな
り地鉄が露出し、この部分が腐
食の起点となる。特に最近のよ
うに錫付着量を少なくしようと
する場合にはこの問題は極めて
深刻になる。この部分の耐食性
を改善するには、塗装前処理で
あるリン酸塩処理が極めて重要
になると考えて本発明者らは検
討を重ねた。リン酸塩皮膜は溶
解性の高い地鉄に優先的に形成
され、ついで錫上に形成される。
ところが、地鉄は溶解性が高す
ぎるためその上に形成されるリ
ン酸塩皮膜は結晶が粗大であ
り、塗装後耐食性は満足のいく
ものではなかった。

特に、錫付着量を少なくした

Usually tin plate used for can bodies, such as
a solder can and a welding can, forms a Fe-Sn
alloy layer by the reflow after the tin plating.
Furthermore a certain chromated treatment is
performed and it is made.

Since it will become short the lifetime of the
metallic mould for DI process if the tin plate for
DI can has a Fe-Sn alloy layer to it, it is an
average not to perform a reflow process.

Moreover, the countermeasure which limits
the surface amount of chromates few from the
relationship of the lifetime of a metallic mould
similarly is also well-known at the unexamined
Japanese patent No. 54-100944.

It was effective in such a technique spreading
the tin plate for DI can.

However, corrosion resistance was halfway
made into the sacrifice.

[PROBLEM ADDRESSED]

When carrying out DI process of the tin plate,
metal tin is eliminated at the time of the drawing
and ironing, a ferrite is exposed, and this part
becomes the origin of a corrosion.

This problem becomes very serious when it is
going to decrease the amount of tin adhesion
like especially recently.

In order to improve corrosion resistance of
this part, the phosphate process which is a pre-
coating process considered that it became very
important, and the present inventors examined
repeatedly.

A phosphate skin layer is preferably formed
on a soluble high ferrite, and, subsequently, is
formed on tin.

However, since solubility of ferrite is too high,
the phosphate skin layer formed on it has the
big and rough crystal.

The corrosion resistance after coating was
not satisfactory.

It becomes very serious when decreasing the
amount of tin adhesion especially.

Then, it investigated about the solubility of a

場合にはそれは極めて深刻になる。そこで、地鉄の溶解性とリン酸塩処理皮膜の関係について調べた。ぶりきの耐食性を改善する方法としては特公昭 57-35276 号や特公昭 54-20940 号がある。

特公昭 57-35276 号はニッケル塩を塗布後焼鈍して Fe-Ni 合金層（ニッケル拡散層）を鋼板表面に形成し、調質圧延後、錫めっきを施すが、リフロー処理は行わないぶりきの製造方法である。しかし、この方法はニッケル塩を還元性雰囲気中で焼鈍することにより金属ニッケルに還元してから鋼中へニッケルが拡散するため鋼板表面のニッケル濃度が高く、その結果、溶解性が悪くなり過ぎて、DI 加工後のリン酸塩処理（塗装下地処理）で化成皮膜の生成速度が露出鉄面と錫被覆面で差がなくなり、錫被覆のない分だけ露出鉄面部で腐食が起こりやすくなり、結果的に塗装後の耐食性は改善されどころかニッケル拡散処理しないものよりも劣っていた。

特公昭 54-20940 号ではニッケルめっきしてから焼鈍するため鋼板表面のニッケル濃度が低く、錫めっき後も常温で合金化は起こりにくい、実施例にもある通りニッケル拡散処理後に酸洗を起っているため鋼板表面の不均一溶解に起因すると思われる汚れが発生する。錫めっき量を 3.0 g/m^2 以上とするか、あるいはリフロー処理を施せばこの外観不良は無くなるが、前者は高価な錫を多く使うために経済的に不利であり、リ

ferrite, and the relationship of a phosphate process skin layer.

As method of improving corrosion resistance of a tin plate, there are Japanese Patent Publication No. 57-35276 and Japanese Patent Publication No. 54-20940.

In Japanese Patent Publication No. 57-35276, after coat-applying a nickel salt, an anneal is carried out, a Fe-Ni alloy layer (nickel diffused layer) is formed on the steel-plate surface, and the tin plating is given after a temper rolling.

However, a reflow process is the manufacturing method of the tin plate not to perform.

However, since a nickel diffuses into steel after reducing to a metal nickel by carrying out the anneal of the nickel salt by the reducing atmosphere, this method has a high nickel concentration on the surface of a steel plate. As a result, solubility becomes bad too much, and the generation rate of a chemical film is eliminated by the phosphate process after DI process (coating surface treatment), and a difference is eliminated in respect of the surface of exposed iron, and tin coating.

Only in the part without a tin coating, a corrosion becomes easy to happen by the exposed iron surface.

As a result, corrosion resistance after coating is improved, not to mention was inferior to that which does not carry out a nickel diffusion process.

In Japanese Patent Publication No. 54-20940, in order to carry out an anneal after carrying out nickel plating, the nickel concentration on the surface of a steel plate is low, and, as for alloying, tin-plating back seldom also happens in normal temperature. However, since the acid wash is happened also to the Example after the nickel diffusion process a certain passage, stain considered to originate in the un-uniform dissolution on the surface of a steel plate generate.

If the amount of tin plating is carried out to more than 3.0 g/m^2 or a reflow process is performed, this poor exterior will be eliminated.

フロー処理を行うと DI 加工時に金型寿命を短くするという問題があった。

錫付着量 0.5～2.0g/m² (片面当り) でも、缶内面の塗装を 1 回に省略できる十分な耐食性の優れた DI 缶用表面処理鋼板は未だない。本発明は、錫付着量を現在より少なくして (2.0g/m² 以下)、かつ内面の塗装回数を 1 回に減らすことが可能な DI 缶用表面処理鋼板の製造方法を提供することを目的としている。

【課題を解決するための手段】

本発明者らはニッケルめっき後焼鈍し、酸洗を施さずに錫めっきすることにより、汚れの如き外観不良のない耐食性と DI 加工性に優れたぶりができることを発見し、詳細な検討を加えて本発明を完成した。

本発明の要旨は下記の通りである。

(1) 塗装後耐食性を改善するために、錫めっき下地としてニッケル濃度の低いニッケル拡散層を設けることにより、リン酸塩処理で露出鉄部に優先的に緻密な化成皮膜が形成されるようにした。

(2) ニッケル拡散処理した鋼板に薄錫めっきして、リフローなしでも良好な外観を得るため、錫めっき前の酸洗を省略した。

(3) 酸洗を省略しても良好な

However, the former is economically disadvantageous in order to use many expensive tin.

When the reflow process was performed, there was a problem of having shortened life of die cast, at the time of DI process.

There is still no surface-treated steel sheet for DI can which tin adhesion quantity 0.5 - 2.0 g/m² (per one side) also excelled in sufficient corrosion resistance which can omit coating of can inner surface once.

This invention decreases the amount of tin adhesion more currently (2.0 g /m² or less). And it aims at providing the manufacturing method of the surface-treated steel sheet for DI can which can reduce the numbers of coats of inner surface once.

[SOLUTION OF THE INVENTION]

By the present inventor's doing an anneal after nickel plating, and carrying out the tin plating, without pickling, it discovered that the tin plate excellent in the corrosion resistance and DI workability with the poor exterior like stain which are not was made, a detailed examination was added, and this invention was perfected.

The gist of this invention is as follows.

(1) In order to improve corrosion resistance after coating, the preferably precise chemical film was made to form by phosphate process by providing the nickel diffused layer with a nickel concentration low as a tin-plating foundation on the exposed iron part.

(2) In order to carry out the thin tin plating to the steel plate which carried out the nickel diffusion process and to obtain a favourable exterior even without a reflow, the acid wash before the tin plating was omitted.

(3) Since the favourable tin plating is made

錫めっきができるように、脱脂、ニッケルめっき、焼鈍、調質圧延、錫めっきを連続的に同一ラインで行うことにした。

すなわち、上記目的を達成するために本発明によれば、薄鋼板を連続的に脱脂、ニッケルめっき、連続焼鈍し、ひきつづきドライ状態で調質圧延し脱脂せずまたは脱脂した後、酸洗を行わず直ちに錫めっきを行うことを特徴とする DI 缶用表面処理鋼板の製造方法が提供される。

また、本発明によれば、薄鋼板を連続的に脱脂、ニッケルめっき、連続焼鈍し、ひきつづきウェット状態で調質圧延した後、脱脂を行い、酸洗を行わず直ちに錫めっきすることを特徴とする DI 缶用表面処理鋼板の製造方法が提供される。

前記ニッケルめっきが、ニッケルを電気めっきにて 0.01~0.5g/m² の付着量で鋼板表面に形成するのが好ましい。

前記連続焼鈍が、還元性雰囲気中で、焼鈍温度 600~900°C、焼鈍時間 10~90 秒で行うのが好ましい。

前記連続焼鈍後の薄鋼板が、表面 Ni 濃度 Ni/(Fe+Ni) (重量比) で 0.02~0.50、厚み 10~5000 Å のニッケル拡散層を形成するのが好ましい。

前記錫めっきが、錫を電気めっきにて 0.5~2.0g/m² の付着量で鋼板表面に形成するのが好ましい。

以下に本発明をさらに詳細に

even when it omits an acid wash, a degreasing, the nickel plating, an anneal, a temper rolling, and the tin plating were made to carrying out with the same line continuously.

Namely, in order to attain the above objective according to this invention, It degreases continuously, and nickel plating of the sheet steel is carried out, and it carries out a continuous annealing. It pulls and a temper rolling is carried out in the continuation dry state, and it does not degrease, or immediately after degreasing, an acid wash is not performed but the tin plating is performed.

The manufacturing method of the surface-treated steel sheet for DI can characterized by the above-mentioned is provided.

Moreover according to this invention, A degreasing, the nickel plating, and immediately after carrying out a continuous annealing, and pulling and carrying out a temper rolling in the state of a continuation wet, continuously, a degreasing is performed, and a sheet steel is not pickled and carries out the tin plating.

The manufacturing method of the surface-treated steel sheet for DI can characterized by the above-mentioned is provided.

It is desirable that the above-mentioned nickel plating forms a nickel on the steel-plate surface in the amount of adhesion of 0.01 - 0.5 g/m² by the electroplating.

~~It is desirable that an above-mentioned continuous annealing carries out in 600-900 degree C of annealing temperatures, and anneal time 10-90 seconds in a reducing atmosphere.~~

It is desirable that the sheet steel after an above-mentioned continuous annealing forms a nickel diffused layer with a thickness of 10-5000 angstroms by surface Ni concentration Ni/(Fe+Ni) (weight ratio) 0.02-0.50, and.

It is desirable that the above-mentioned tin plating forms tin on the steel-plate surface in the amount of adhesion of 0.5 - 2.0 g/m² by the electroplating.

This invention is demonstrated even in detail below.

説明する。

本発明において用いる薄鋼板は、冷間圧延鋼板である。

冷間圧延された鋼板は圧延油が多量に付着しているため、ニッケルめっきを行う前に脱脂される。この脱脂は、界面活性剤を含むアルカリ水溶液中で陰極電解、陽極電解あるいはそれらを組合せて電解する通常の電解脱脂でよい。

脱脂後、ニッケルめっき前に酸洗を行ってもよく、本発明により得られる製品の品質に影響を与えるものではない。しかし、酸洗は設備の大型化につながり、経済的に不利であるため、省略するのが得策である。

ニッケルめっきは、Ni 付着量が重要であり 0.01~0.5g/m² の範囲に限定することが好ましい。Ni 付着量が 0.01g/m² より少ないと焼鈍後に必要な表面 Ni 濃度に満たなくなり、ひいては十分な耐食性が得られない。また、Ni 付着量が 0.5g/m² より多いと、焼鈍後に表面 Ni 濃度が最大となる表面近傍での表面 Ni 濃度が Ni/(Fe+Ni) (重量比) で 50% を超え、DI 加工後のリン酸塩処理時に露出鉄部に優先的に緻密なリン酸塩皮膜が生成しないため、錫被覆のない分だけ露出鉄部で腐食が起こりやすくなり、やはり十分な塗装後耐食性が得られない。Ni 付着量が 0.01~0.5g/m² の場合には、表面 Ni 濃度の最大値が 50% を超えないので、錫被覆部より露出鉄部に優先的にリン酸塩皮膜が生成し、

The sheet steel used in this invention is a cold rolled steel plate.

Since the rolling oil has adhered so much, the steel plate which is cold-rolled is degreased before performing nickel plating.

This degreasing is good at the usual electrolytic degreasing which combines and electrolyzes cathode electrolysis, anode electrolysis, or them in the alkaline-water solution containing a surfactant.

It may pickle after a degreasing and before the nickel plating. Influence is not imparted in the quality of the product obtained by this invention.

However, an acid wash is connected with an expansion of an installation, and since it is economically disadvantageous, a best policy omits.

The amount of Ni adhesion is important for the nickel plating, and; as for it, it is desirable to limit to the range of 0.01 - 0.5 g/m².

If the amount of Ni adhesion is fewer than 0.01 g/m²s, it will stop fulfilling a surface Ni concentration required after an anneal.

As a result sufficient corrosion resistance is not obtained.

Moreover, if there are many amounts of Ni adhesion from 0.5 g/m²s, the surface Ni concentration near where a surface Ni concentration becomes the maximum after an anneal the surface will exceed 50% by Ni/(Fe+Ni) (weight ratio). In order that a preferably precise phosphate skin layer may not form to an exposed iron part at the time of the phosphate process after DI process, only in the part without a tin coating, a corrosion becomes easy to happen by the exposed iron part.

As expected sufficient corrosion resistance after coating is not obtained.

When the amount of Ni adhesion is 0.01 - 0.5 g/m², the maximum of a surface Ni concentration does not exceed 50%. Therefore, a phosphate skin layer preferably forms from a tin coating part to an exposed iron part. And since it is precise to the same extent as a tin

しかもそれが錫被覆部と同程度に緻密であるので、非常に優れた塗装後耐食性を示す。

焼鈍条件は、水素ガスを含む還元性雰囲気中、焼鈍温度 600～900℃、焼鈍時間 10～90 秒の連続焼鈍で行うことが好ましい。雰囲気が水素ガスを含まず、単に無酸化性であるだけでは、焼鈍前、あるいは焼鈍時に生成した酸化膜が、調質圧延後の錫めっきの均一電着性を阻害する。還元性雰囲気としては通常の水素と窒素の混合ガスであればよい。焼鈍温度が 600℃より低い場合、または焼鈍時間が 10 秒より短い場合にはめっきされたニッケルが鋼中に十分に拡散せず、焼鈍後の表面ニッケル濃度の最大値が 50%を超えるため、露出鉄部のリン酸塩皮膜が不十分となり、塗装後耐食性に劣る。焼鈍温度が 900℃を超える場合、または焼鈍時間が 90 秒を超える場合には焼鈍後の表面ニッケル濃度が 2%より低くなるため、露出鉄部のリン酸塩皮膜が粗大となり、やはり塗装後耐食性に劣る。

調質圧延は特に限定する必要はなく、所望の材質や板厚に応じて圧下率を決定すればよく、通常 0.5～60%の範囲である。圧下率が数%を超えない場合には圧延油を必要としないドライ調質圧延でもよいが、圧下率が数%を超える場合には圧延油を使用するウェット調質圧延が望ましい。

調質圧延後、錫めっきを行う前に脱脂は適宜行うが、酸洗は行ってはならない。ドライ調質

coating part, the corrosion resistance after coating which was very excellent is shown.

As for anneal conditions, it is desirable to carry out by the continuous annealing for 600-900 degree C of annealing temperatures and anneal time 10-90 seconds among the reducing atmosphere containing hydrogen gas.

The oxide film which atmosphere formed before the anneal only by it being deoxidization property excluding hydrogen gas at the time of an anneal inhibits throwing power of the tin plating after a temper rolling.

What is sufficient is just to be mixed gas of usual hydrogen and nitrogen as a reducing atmosphere.

When an annealing temperature is lower than 600 degree C, or when an anneal time is shorter than 10 seconds, the nickel by which the plating was carried out does not diffuse sufficiently in steel. In order that the maximum of the surface nickel concentration after an anneal may exceed 50%, the phosphate skin layer of an exposed iron part becomes inadequate.

It is inferior to the corrosion resistance after coating.

Since the surface nickel concentration after an anneal becomes lower than 2% when an annealing temperature exceeds 900 degree C, or when an anneal time exceeds 90 seconds, the phosphate skin layer of an exposed iron part becomes big and rough.

It is inferior to the corrosion resistance after coating as expected.

Especially a temper rolling is 0.5-60% of a usual range that what is sufficient is just not to limit and to determine a draft percentage depending on a desired material or a thickness.

Although the dry temper rolling which does not need a rolling oil may be used when a draft percentage does not exceed a several percent, when a draft percentage exceeds a several percent, the wet temper rolling which uses a rolling oil is desirable.

After a temper rolling, before performing the tin plating, a degreasing is performed suitably.

However, an acid wash must not be

圧延の場合には脱脂は特に必要ないがウェット調質圧延の場合には脱脂は必要である。この脱脂は、通常の界面活性剤を含むアルカリ水溶液中での陰極電解、陽極電解、あるいはこれらを混合した電解で良く、特に限定する必要はない。同じめっき前処理でも脱脂と異なり、酸洗はこの場合行ってはならない。酸洗を行うと、ニッケル拡散処理した鋼板の不均一溶解に起因すると考えられる汚れ状の外観不良を起こす。この汚れは薄錫めっき後も残るので外観不良で商品価値がない。したがって、錫めっき前には、酸洗を絶対に行ってはならない。酸洗を省略するためには、ニッケル拡散処理後速やかに錫めっきを行う必要がある。ニッケル拡散処理後、防錆油を塗布して置いた場合には、30分程度までは酸洗なしでも良好な錫めっきができないこともないが、コイル単位でめっきするため、物流の関係から現実的でない。したがって、ニッケル拡散処理、調質圧延、錫めっきは同一ラインにて連続的に行わなければならない。

錫付着量は $0.5 \sim 2.0 \text{ g/m}^2$ の範囲が好ましい。錫付着量が 0.5 g/m^2 より少ないと満足なDI加工ができない。錫付着量が 2.0 g/m^2 を超えても品質上の問題はないが、錫付着量を多くすることは経済的に不利である。錫めっき方法は特に限定する必要はなく、従来の錫めっき

performed.

The degreasing is required, when it is a wet temper rolling, although a degreasing does not have the need specifically in the case of a dry temper rolling.

Cathode electrolysis in the alkaline-water solution containing a usual surfactant, anode electrolysis, or electrolysis which mixed these is sufficient as this degreasing, and it does not need to be limited especially.

The same plating preprocessing also differs from a degreasing.

An acid wash must not be performed in this case.

An acid wash causes the poor exterior of the stain considered to originate in un-uniform dissolution of a steel plate which carried out the nickel diffusion process.

Since thin tin-plating back also remains, the exterior of this stain is poor and it does not have a commercial value.

Therefore, before the tin plating, it must not pickle by any means.

In order to omit an acid wash, the tin plating needs to be quickly performed after a nickel diffusion process.

When rust-proof oil is applied a coating and put after a nickel diffusion process, the favourable tin plating is not made even without an acid wash till about 30 minutes.

However, in order to carry out a plating per coil, it is not realistic from the relationship of an object flow.

Therefore, a nickel diffusion process, a temper rolling, and the tin plating must be continuously performed with the same line.

The amount of tin adhesion has the desirable range of $0.5 - 2.0 \text{ g/m}^2$.

If the amount of tin adhesion is fewer than 0.5 g/m^2 s, satisfactory DI process will not be made.

Even when the amount of tin adhesion exceeds 2.0 g/m^2 s, there is no problem on quality.

However, it is economically disadvantageous to make many the amount of tin adhesion.

Especially the tin-plating method does not

浴、例えばハロゲン浴、フェロスタン浴、アルカリ浴、ホウ弗化浴などを使用すればよい。

錫めっき後は、リフロー処理を行わない。これは Fe-Sn 合金層は固いために、DI 加工用の金型の寿命を短くすることによる。

錫めっきの上にクロメート処理を行うと、リフロー処理と同じように DI 加工用金型の寿命を短くするのでクロメート処理は行わないのがよい。クロメート処理を省くことによって保管時の錫酸化膜の成長が懸念されるが、リフロー処理を行わない場合には錫酸化膜は極少量で飽和になるのでその心配がない。

【実施例】

以下に本発明を実施例に基づき具体的に説明する。

【実施例 1】

冷延鋼板を電解脱脂し、水洗した後、 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240g/l、 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45g/l、 H_3BO_3 30g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.1g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。

引き続き、脱脂・酸洗を行わずに直ちに、 SnCl_2 75g/l、 NaF 25g/l、 $\text{KF} \cdot \text{HF}$ 50g/l、 NaCl 40g/l、 Sn^{2+} 36g/l、

need to be limited and should just use the conventional tin-plating bath, for example, halogen bath, ferrotan bath, an alkaline-bath fluoroborate bath, etc.

After the tin plating does not perform a reflow process.

Since this of a Fe-Sn alloy layer is hard, it is based on shortening the lifetime of the metallic mould for DI process.

If a chromated treatment is performed on the tin plating, since the lifetime of the metallic mould for DI process will be shortened like a reflow process, as for a chromated treatment, not carrying out is good.

It is anxious about the growth of the stannic-acid-ized membrane at the time of storage by excluding a chromated treatment.

However, in not performing a reflow process, since a stannic-acid-ized membrane becomes a saturation with small amount very, it does not have the worries.

【Example】

This invention is concretely demonstrated below based on an Example.

【Example 1】

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45 g/l, H_3BO_3 30 g/l, pH4.0, and the temperature of 50 degree C.

An anneal is immediately carried out in a reducing atmosphere (10% H₂, 25 degree C of dew points, remainder N₂), the temperature of 700 degree C and time 30 seconds after wash in water * drying. The dry temper rolling of 1% of draft percentages was carried out succeedinglly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a

Sn4+ 1g/l、PH2. 7、添加剤 1g/l、温度 65°Cで鋼板を陰極として電流密度 50A/dm²、電解時間 0. 4 秒の電気錫めっき (Sn 付着量 1. 2g/m²) を施し、水洗・乾燥して供試材とした。

【実施例 2】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄ · 7H₂O 240g/l、NiCl₂ · 6H₂O 45g/l、H₃BO₃30g/l、pH4. 0、温度 50°Cで鋼板を陰極として電流密度 30A/dm²、電解時間 1. 2 秒の電気ニッケルめっき (Ni 付着量 0. 4g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、0. 05% CO₂、0. 05% Co、trace CH₄ 露点 - 40°C、残部 N₂)、温度 850°C、時間 45 秒で焼鈍し、引き続き圧下率 50%のウェット調質圧延をした。引き続き、アルカリ電解脱脂後、水洗し、酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF · HF 50g/l、NaCl 40g/l、Sn2+ 36g/l、Sn4+ 1g/l、pH2. 7、添加剤 1g/l、温度 65°Cで鋼板を陰極として電流密度 50A/dm²、電解時間 0. 4 秒の電気錫めっき (Sn 付着量 1. 2g/m²) を施し、水洗・乾燥して供試材とした。

【実施例 3】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄ · 7H₂O 240g/l、NiCl₂ · 6H₂O 45g/l、H₃BO₃30g/l、pH4. 0、温度 50°Cで鋼板を陰極として電流

cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF·HF 50 g/l, NaCl 40 g/l, Sn2+36 g/l, Sn4+1 g/l, PH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Example 2]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 30A/dm², and electrolysis time 1.2 seconds (amount of Ni adhesion 0.4 g/m²) is performed, using a steel plate as a cathode at NiSO₄·7H₂O 240 g/l, NiCl₂·6H₂O 45 g/l, H₃BO₃30 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, 0.05% CO₂, 0.05% Co, - 40 degree C of dew points, trace CH₄ remainder N₂), ~~the temperature of 850 degree C and time 45 seconds.~~ The wet temper rolling of 50% of draft percentages was carried out succeedinglly.

Then, it washes in water after an alkali electrolytic degreasing. It does not pickle. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF·HF 50 g/l, NaCl 40 g/l, Sn2+36 g/l, Sn4+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Example 3]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 30A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.2 g/m²) is performed, using a steel plate as a cathode at

密度 30A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.2g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 650°C、時間 60 秒で焼鈍し、引き続き圧下率 1% のウェット調質圧延をした。引き続き、アルカリ電解脱脂後、水洗し、酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF·HF 50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.2g/m²) を施し、水洗・乾燥して供試材とした。

【実施例 4】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄·7H₂O 240g/l、NiCl₂·6H₂O 45g/l、H₃BO₃30g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.1g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き、アルカリ電解脱脂後、水洗し、酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF·HF 50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.

NiSO₄·7H₂O 240 g/l, NiCl₂·6H₂O 45 g/l, H₃BO₃30 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 650 degree C, and time 60 seconds. The wet temper rolling of 1% of draft percentages was carried out succeedingly.

Then, it washes in water after an alkali electrolytic degreasing. It does not pickle. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF·HF 50 g/l, NaCl 40 g/l, Sn²⁺36 g/l, Sn⁴⁺1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Example 4]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at NiSO₄·7H₂O 240 g/l, NiCl₂·6H₂O 45 g/l, H₃BO₃30 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds. The dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, after an alkali electrolytic degreasing, It washes in water. It does not pickle. Immediately, the electric tin plating (amount of Sn adhesion 1.8 g/m²) for current-density 50A/dm², and electrolysis time 0.6 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF·HF 50 g/l, NaCl 40 g/l, Sn²⁺36 g/l, Sn⁴⁺1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water

6 秒の電気錫めっき (Sn 付着量 1. 8g/m²) を施し、水洗・乾燥して供試材とした。

* dried and it used as the material.

【実施例 5】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄・7H₂O 240g/l、NiCl₂・6H₂O 45g/l、H₃BO₃330g/l、pH4. 0、温度 50℃で鋼板を陰極として電流密度 30A/dm²、電解時間 0. 9 秒の電気ニッケルめっき (Ni 付着量 0. 3g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10%H₂、0. 05%Co₂、0. 05%Co、trace CH₄ 露点 -40℃、残部 N₂)、温度 800℃、時間 45 秒で焼鈍し、引き続き圧下率 15%のウェット調質圧延をした。引き続き、アルカリ電解脱脂後、水洗し、酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF・HF 50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2. 7、添加剤 1g/l、温度 65℃で鋼板を陰極として電流密度 25A/dm²、電解時間 0. 6 秒の電気錫めっき (Sn 付着量 0. 6g/m²) を施し、水洗・乾燥して供試材とした。

【比較例 1】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄・7H₂O 240g/l、NiCl₂・6H₂O 45g/l、H₃BO₃330g/l、pH4. 0、温度 50℃で鋼板を陰極として電流密度 15A/dm²、電解時間 0. 06 秒の電気ニッケルめっき (Ni 付着量 0. 01g/m²) を施して、水洗・乾燥後、直ちに還元性雰

【Example 5】

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 30A/dm², and electrolysis time 0.9 seconds (amount of Ni adhesion 0.3 g/m²) is performed, using a steel plate as a cathode at NiSO₄·7H₂O 240 g/l, NiCl₂·6H₂O 45 g/l, H₃BO₃330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (-40 dew points of 10% H₂, 0.05% Co₂, 0.05% Co and trace CH₄ dew points, remainder N₂), ~~the temperature of 800 degree C, and time 45 seconds.~~ The wet temper rolling of 15% of draft percentages was carried out succeedingly.

Then, it washes in water after an alkali electrolytic degreasing. It does not pickle. Immediately, the electric tin plating (amount of Sn adhesion 0.6 g/m²) for current-density 25A/dm², and electrolysis time 0.6 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF·HF 50 g/l, NaCl 40 g/l, Sn²⁺+36 g/l, Sn⁴⁺+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

【Comparative Example 1】

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.06 seconds (amount of Ni adhesion 0.01 g/m²) is performed, using a steel plate as a cathode at NiSO₄·7H₂O 240 g/l, NiCl₂·6H₂O 45 g/l, H₃BO₃330 g/l, pH4.0, and the temperature of 50 degree C.

After wash in water * drying, An anneal is

雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF・HF 50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.28/m²) を施し、水洗・乾燥して供試材とした。

【比較例 2】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄・7H₂O 240g/l、NiCl₂・6H₂O 45g/l、H₃B₃O₃ 330g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 4.2 秒の電気ニッケルめっき (Ni 付着量 0.7g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。

引き続き、脱脂・酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF・HF 50g/l、NaCl 40g/l、S₂O₂ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.2g/m²) を施し、水洗・乾燥して供試材とした。

【比較例 3】

immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds. The dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.28/square meter) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF 50 g/l, NaCl 40 g/l, Sn²⁺+36 g/l, Sn⁴⁺+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 2]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 4.2 seconds (amount of Ni adhesion 0.7 g/m²) is performed, using a steel plate as a cathode at NiSO₄*7H₂O 240 g/l, NiCl₂*6H₂O 45 g/l, H₃B₃O₃ 330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds. The dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF 50 g/l, NaCl 40 g/l, S₂O₂+36 g/l, Sn⁴⁺+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 3]

冷延鋼板を電解脱脂し、水洗した後、 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240g/l、 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45g/l、 H_3BO_3 330g/l、pH4.0、温度50°Cで鋼板を陰極として電流密度15A/dm²、電解時間0.6秒の電気ニッケルめっき（Ni付着量0.1g/m²）を施して、水洗・乾燥後、直ちに還元性雰囲気（10% H₂、露点-25°C、残部N₂）、温度500°C、時間30秒で焼鈍し、引き続き圧下率1%のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、 SnCl_2 75g/l、NaF 25g/l、 $\text{KF} \cdot \text{HF}$ 50g/l、NaCl 40g/l、 Sn^{2+} 36g/l、 Sn^{4+} 1g/l、pH2.7、添加剤1g/l、温度65°Cで鋼板を陰極として電流密度50A/dm²、電解時間0.4秒の電気錫めっき（Sn付着量1.2g/m²）を施し、水洗・乾燥して供試材とした。

【比較例 4】

冷延鋼板を電解脱脂し、水洗した後、 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240g/l、 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45g/l、 H_3BO_3 330g/l、pH4.0、温度50°Cで鋼板を陰極として電流密度15A/dm²、電解時間0.6秒の電気ニッケルめっき（Ni付着量0.1g/m²）を施して、水洗・乾燥後、直ちに還元性雰囲気（10% H₂、露点-25°C、残部N₂）、温度700°C、時間5秒で焼鈍し、引き続き圧下率1%のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、 SnCl_2 75g/l、NaF 25g/l、 $\text{KF} \cdot \text{HF}$ 50g/l、NaCl 40g/l、 Sn^{2+} 36g/l、 Sn^{4+} 1g

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45 g/l, H_3BO_3 330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 500 degree C, and time 30 seconds. The dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl_2 75 g/l, NaF 25 g/l, $\text{KF} \cdot \text{HF}$ 50 g/l, NaCl 40 g/l, Sn^{2+} 36 g/l, Sn^{4+} 1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 4]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45 g/l, H_3BO_3 330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, An anneal is immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 5 seconds. The dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4

／l、pH2. 7、添加剤 1g／l、温度 65℃で鋼板を陰極として電流密度 50A／dm²、電解時間 0. 4 秒の電気錫めっき (Sn 付着量 1. 2g／m²) を施し、水洗・乾燥して供試材とした。

【比較例 5】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄・7H₂O 240g／l、NiCl₂・6H₂O 45g／l、H₃BO₃330g／l、pH4. 0、温度 50℃で鋼板を陰極として電流密度 15A／dm²、電解時間 0. 6 秒の電気ニッケルめっき (Ni 付着量 0. 1g／m²) を施して、水洗・乾燥後、直ちに非還元性雰囲気 (露点 -25℃、N₂)、温度 700℃、時間 30 秒で焼鈍し、引き続き圧下率 1%のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、SnCl₂ 75g／l、NaF 25g／l、KF・HF 50g／l、NaCl40g／l、Sn²⁺ + 36g／l、Sn⁴⁺ + 1g／l、pH2. 7、添加剤 1g／l、温度 65℃で鋼板を陰極として電流密度 50A／dm²、電解時間 0. 4 秒の電気錫めっき (Sn 付着量 1. 2g／m²) を施し、水洗・乾燥して供試材とした。

【比較例 6】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄・7H₂O 240g／l、NiCl₂・6H₂O 45g／l、H₃BO₃330g／l、pH4. 0、温度 50℃で鋼板を陰極として電流密度 15A／dm²、電解時間 0. 6 秒の電気ニッケルめっき (Ni 付着量 0. 1g／m²) を施して、水洗・乾燥後、直ちに還元性雰囲気

seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF 50 g/l, NaCl 40 g/l, Sn²⁺+36 g/l, Sn⁴⁺+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 5]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at NiSO₄*7H₂O 240 g/l, NiCl₂*6H₂O 45 g/l, H₃BO₃330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, the anneal was immediately carried out in a non-reducing atmosphere (-25 degree C of dew points, N₂), the temperature of 700 degree C, and time 30 seconds, and the dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF 50 g/l, NaCl40 g/l, Sn²⁺+36 g/l, Sn⁴⁺+1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 6]

The electrolytic degreasing of the cold rolled sheet steel is carried out. After washing in water, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at NiSO₄*7H₂O 240 g/l, NiCl₂*6H₂O 45 g/l, H₃BO₃330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, the anneal was immediately carried out in a

気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに、5% 硫酸、50°C 中で電解酸洗して、水洗後直ちに、SnCl₂ 75g/l、NaF 25g/l、KF・HF50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.2g/m²) を施し、水洗・乾燥して供試材とした。

【比較例 7】

冷延鋼板を電解脱脂し、水洗した後、NiSO₄·7H₂O 240g/l、NiCl₂·6H₂O 45g/l、H₃BO₃ 30g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.1g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、SnCl₂ 75g/l、NaF 25g/l、KF・HF50g/l、NaCl 40g/l、Sn²⁺ 36g/l、Sn⁴⁺ 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 0.3g/m²) を施し、水洗・乾燥して供試材とした。

reducing atmosphere (-25 dew points of 10% H₂ and dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds, and the dry temper rolling of 1% of draft percentages was carried out succeedingly. Then, an electrolytic pickling is carried out in 5% sulfuric acid and 50 degree C, without performing a degreasing * acid wash.

After wash in water immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF50 g/l, NaCl 40 g/l, Sn²⁺36 g/l, Sn⁴⁺1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

[Comparative Example 7]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at NiSO₄*7H₂O 240 g/l, NiCl₂*6H₂O 45 g/l, H₃BO₃ 30 g/l, pH4.0, and the temperature of 50 degree C.

After wash in water * drying, the anneal was immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds, and the dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 0.3 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl₂ 75 g/l, NaF 25 g/l, KF*HF50 g/l, NaCl 40 g/l, Sn²⁺36 g/l, Sn⁴⁺1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. It washed in water * dried and it used as the material.

【比較例 8】

冷延鋼板を電解脱脂し、水洗した後、 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240g/l、 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45g/l、 H_3BO_3 330g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.1g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き、脱脂・酸洗を行わずに直ちに、 SnCl_2 75g/l、NaF 25g/l、 $\text{KF} \cdot \text{HF}$ 50g/l、NaCl 40g/l、 Sn^{2+} 36g/l、 Sn^{4+} 1g/l、pH2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.2g/m²) を施し、水洗後、リフロー処理を施して鉄錫合金層 (合金 Sn 量 0.4g/m²) を形成してから水洗・乾燥して供試材とした。

【比較例 9】

冷延鋼板を電解脱脂し、水洗した後、 $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240g/l、 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45g/l、 H_3BO_3 330g/l、pH4.0、温度 50°C で鋼板を陰極として電流密度 15A/dm²、電解時間 0.6 秒の電気ニッケルめっき (Ni 付着量 0.1g/m²) を施して、水洗・乾燥後、直ちに還元性雰囲気 (10% H₂、露点 -25°C、残部 N₂)、温度 700°C、時間 30 秒で焼鈍し、引き続き圧下率 1% のドライ調質圧延をした。引き続き

[Comparative Example 8]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45 g/l, H_3BO_3 330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, the anneal was immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds, and the dry temper rolling of 1% of draft percentages was carried out succeedingly.

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl_2 75 g/l, NaF 25 g/l, $\text{KF} \cdot \text{HF}$ 50 g/l, NaCl 40 g/l, Sn^{2+} 36 g/l, Sn^{4+} 1 g/l, pH2.7, additive 1 g/l, and the temperature of 65 degree C. After having performed the reflow process and having formed the iron tin-alloy layer (amount of alloy Sn 0.4 g/m²), after wash in water, it wash in water * Dried and it used as the material.

[Comparative Example 9]

After carrying out the electrolytic degreasing of the cold rolled sheet steel, and washing in water it, Electric nickel plating for current-density 15A/dm², and electrolysis time 0.6 seconds (amount of Ni adhesion 0.1 g/m²) is performed, using a steel plate as a cathode at $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 45 g/l, H_3BO_3 330 g/l, pH4.0, and the temperature of 50 degree C. After wash in water * drying, the anneal was immediately carried out in a reducing atmosphere (10% H₂, -25 degree C of dew points, remainder N₂), the temperature of 700 degree C, and time 30 seconds, and the dry temper rolling of 1% of draft percentages was carried out succeedingly.

き、脱脂・酸洗を行わずに直ちに、 SnCl_2 75g/l、 NaF 25g/l、 $\text{KF} \cdot \text{HF}$ 50g/l、 NaCl 40g/l、 Sn^{2+} 36g/l、 Sn^{4+} 1g/l、 pH 2.7、添加剤 1g/l、温度 65°C で鋼板を陰極として電流密度 50A/dm²、電解時間 0.4 秒の電気錫めっき (Sn 付着量 1.2g/m²) を施し、水洗後、 Na_2CrO_4 30g/l、 pH 5、温度 55°C で鋼板を陰極として電流密度 5A/dm²、電解時間 1 秒のクロメート処理を施し、水洗・乾燥して供試材とした。

以上のようにして得られた両面メッキした供試材は下記の如く評価した。

【錫均一電着性】

走査型電子顕微鏡 (1000 倍) により観察して、以下の通り判定した。

不可・・・錫の電着していない部分が 5% 超を占める。

可・・・錫の電着していない部分が 1% 超 5% 以下である。

良好・・・錫の電着していない部分が 1% 以下である。

【製缶前耐錆性】

製缶前耐錆性は、屋内で暴露して発錆状況を次のように判定した。

不可・・・6 日以内に 1dm² 当り 1 個以上の点錆発生

可・・・7 日以上 13 日以内に 1dm² 当り 1 個以上の点錆発生

良好・・・14 日で 1dm² 当り 1 個以上の点錆発生なし

【DI 加工性】

Then, a degreasing * acid wash is not performed. Immediately, the electric tin plating (amount of Sn adhesion 1.2 g/m²) for current-density 50A/dm², and electrolysis time 0.4 seconds is given, using a steel plate as a cathode at SnCl_2 75 g/l, NaF 25 g/l, $\text{KF} \cdot \text{HF}$ 50 g/l, NaCl 40 g/l, Sn^{2+} 36 g/l, Sn^{4+} 1 g/l, pH 2.7, additive 1 g/l, and the temperature of 65 degree C. The chromated treatment for current-density 5A/dm², and electrolysis time 1 second is performed after wash in water, using a steel plate as a cathode at Na_2CrO_4 30 g/l, pH 5, and the temperature of 55 degree C. It washed in water * dried and it used as the material.

The material which is above and was obtained by making and which carried out double-sided plating was evaluated as follows.

[Tin throwing power]

It observes by the scanning-type electronic microscope (1000 increment).

It judged as follows.

Improper *** The part which has not electrodeposited tin occupies over 5%.

Good *** The part which has not electrodeposited tin is 1% over 5% or less.

Favourable *** The part which has not electrodeposited tin is a 1% or less.

[before canning rusting proof]

Before canning rusting proof was exposed indoors and judged the rust situation as follows.

Improper *** It will generate 1 or more point-like rust per 1dm² in less than 6 days.

Good *** It will generate 1 or more point-like rust per 1dm² in less than 13 days 7 days or more.

Favourable *** It will have no 1 or more point-like rust generation per 1dm² at 14 days.

[DI workability]

不可・・・DI加工時に破断するか、またはストリップイング時に座屈するもの

不良・・・DI加工はできるが、金型の損傷が激しいもの

可・・・DI加工ができ、金型の損傷が軽いもの

良好・・・DI加工ができ、目に見える金型の損傷がないもの

Improper *** That which is fractured at the time of DI process, or carries out a buckling at the time of a stripping

Defect *** DI process is made. However, what has intense damage of a metallic mould

Good *** DI process is made and it is thing with light damage of a metallic mould.

Favourable *** That which DI process is made and does not have damage of the metallic mould which is visible to an eye

【リン酸塩処理皮膜の地鉄被覆性】

リン酸塩処理皮膜の被覆状況は走査電子顕微鏡(1000倍)とEPMAを使って調べられるが、最終的には錫とリン酸塩皮膜を合せた地鉄面の被覆が重要であるから、鉄露出量を測定するのが実用的である。それには、下記のIEVが最も適切であり、かつ簡便である。

DI成形された缶体は、弱アルカリクリーナー(ファインクリーナー4361A、日本バーカライジング製)でスプレー法により脱脂し、水洗後、クロムフリーフッ素フリーのリン酸塩処理剤(PF-K3482、日本バーカライジング製)でスプレー法によりP付着量1.1mg/m²のリン酸塩皮膜を形成した。

リン酸塩皮膜の地鉄被覆性は、上記缶体の缶胴中央部から試験片を切り出して、IEV(Iron Exposure Value 鉄露出値: 第2回ぶりき国際会議、1980年、ロンドン、PaperNo. 31、M. Tsurumaru 他)により判定した。

不可・・・IEV200mA超

可・・・IEV50mA超 200mA

[Ferrite coating property of a phosphate process skin layer]

The coating situation of a phosphate process skin layer is investigated using a scanning electron microscope (1000 increment) and EPMA.

However, since the coating of a ferrite surface which finally united the phosphate skin layer with tin is important, it is practical to measure an iron exposure.

IEV of the following is the most suitable for it.

And it is simple.

The can by which DI shaping was carried out is degreased by the spray method with a weak alkali cleaner (fine cleaner 4361A, Japanese barker rising manufacturing). The phosphate skin layer with an amount of P adhesion of 1.1 mg/square meter was formed by the spray method by chrome free fluorine free's phosphate process agent (PF-K3482, Japanese barker rising manufacturing) after wash in water.

The ferrite coating property of a phosphate skin layer cuts down a test piece from the can-body center section of an above can.

IEV (an Iron Exposure Value iron exposure-value: second time tin-plate international meeting, 1980 London Paper No.31 and M.Tsurumaru et al.) It judged by above.

Improper *** IEV200mA over Good ***
 IEV50mA over less200mA Favourable ***
 Less than IEV50mA

以下

良好・・・IEV50mA 以下

【内面塗装後耐食性】

上記のリン酸塩処理した缶体の内面にエポキシアミノ系塗料をスプレー法により 60mg/dm² 塗布・焼付けした後、缶胴部を切り出して端部をシールしてから、クロスカットを入れ、クエン酸 15% + 食塩 15%、55℃の液に 96 時間浸漬して、クロスカット部の幅方向および深さ方向の腐食状況を創造的に判断して、良好、可、不可の 3 段階で評価した。

【外面缶底耐錆性】

上記内面塗装した缶体を使って、缶外面の底部に塗装することなく、JIS z 2371 に定められた方法で、12 時間塩水噴霧試験して赤錆の発生状況により判定した。

不可・・・全面に赤錆発生
 可・・・少数の赤錆発生
 良好・・・赤錆発生無し

表-1 に供試材の製造条件と品質特性を一覧表にして示した。

比較例 1 は、Ni 付着量が 0.01g/m² と少ないために、鋼板の表面 Ni 濃度が 1% と低くなり過ぎ、その結果リン酸塩処理性が劣り、十分な内面塗装後耐食性が得られなかった。

比較例 2 は、Ni 付着量が 0.70g/m² と多いために、鋼板の表面 Ni 濃度の最大値が 100% と

[Corrosion resistance after inner surface coating]

To Above-mentioned inner surface of the can which carried out the phosphate process It carried out by coat-application * Printing an epoxy amino group coating material 60 mg/dm² by the spray method. Back, after cutting a can-body part out and sealing an edge part, a cross cut is put. It immerses to 15% of salt + 15% of citric acids, and a 55 degree C liquid for 96 hours.

The corrosion situation of the cross direction of a cross-cut part and the depth direction is judged creatively.

Favourable and three good and improper stages evaluated.

[Outside can-bottom rusting proof]

The can which carried out above inner surface coating is used.

Without coating at the bottom part of the can outer surface, by the method set to JIS z 2371, the salt spray test was carried out for 12 hours, and it judged according to the generation situation of rust.

Improper *** It is rust generation entirely.
 Good *** A small number of rust generation Favourable *** Rust generation none

The manufacture conditions and the quality characteristic of a material were used as the chart, and were shown in Table-1.

Since Comparative Example 1 has the amount as few as 0.01 g/m²s of Ni adhesion, the surface Ni concentration of a steel plate becomes as low as 1% too much, and as a result, a phosphate processability is inferior, and sufficient corrosion resistance after inner surface coating was not obtained.

Since Comparative Example 2 has many amounts of Ni adhesion as 0.70 g/m²s, the maximum of the surface Ni concentration of a steel plate becomes as high as 100% too much.

高くなり過ぎ、その結果リン酸塩処理性が劣り、十分な内面塗装後耐食性が得られなかった。

比較例 3 は、焼鈍温度が 500°C と低過ぎるために、Ni が十分に拡散することができず、鋼板の表面 Ni 濃度の最大値が 60% と高くなり過ぎ、その結果リン酸塩処理性が劣り、十分な内面塗装後耐食性が得られなかった。

比較例 4 は、焼鈍時間が 5 秒と短過ぎるために、Ni が十分に拡散することができず、鋼板の表面 Ni 濃度の最大値が 70% と高くなり過ぎ、その結果リン酸塩処理性が劣り、十分な内面塗装後耐食性が得られなかった。

比較例 5 は、焼鈍が還元性雰囲気ではないために、錫めっき外観、錫均一電着性が劣るだけでなく、地鉄酸化膜の存在のゆえにリン酸塩処理性が劣り、やはり十分な内面塗装後耐食性が得られなかった。

比較例 6 は、Ni 拡散処理後錫めっき前に酸洗を行っているために外観不良となった。

比較例 6 は、Ni 拡散処理後錫めっき前に酸洗を行っているために外観不良となった。

比較例 7 は、錫付着量が 0.3g/m² と少過ぎるために十分な DI 加工ができなかった。

比較例 8 は、錫めっき後、リフロー処理を行って、鉄錫合金層を形成しているために、DI 加工そのものは可能であるが、金型の損傷が大きく、実用的でない。

As a result, a phosphate processability is inferior, and sufficient corrosion resistance after inner surface coating was not obtained.

Since Comparative Example 3 has an annealing temperature too as low as 500 degree C, Ni cannot diffuse it sufficiently, but the maximum of the surface Ni concentration of a steel plate becomes 60% high too much. As a result, a phosphate processability is inferior, and sufficient corrosion resistance after inner surface coating was not obtained.

Since Comparative Example 4 has an anneal time too as short as 5 seconds, Ni cannot diffuse it sufficiently, but the maximum of the surface Ni concentration of a steel plate becomes 70% high too much. As a result, a phosphate processability is inferior, and sufficient corrosion resistance after inner surface coating was not obtained.

Since an anneal is not a reducing atmosphere, a tin-plating exterior and tin throwing power are not only inferior, but Comparative Example 5 is inferior in a phosphate processability on account of the existence of a ferrite oxide film. As expected sufficient corrosion resistance after inner surface coating was not obtained.

Since it was pickling after Ni diffusion process and before the tin plating, Comparative Example 6 became poor exterior.

Since it was pickling after Ni diffusion process and before the tin plating, Comparative Example 6 became poor exterior.

Since Comparative Example 7 had the amount too as few as 0.3 g/m²s of tin adhesion, it was not able to do sufficient DI process.

Comparative Example 8 is performing the reflow process after the tin plating.

Since an iron tin-alloy layer is formed, the DI process itself is possible.

However, damage of a metallic mould is large and is not practical.

比較例 9 は、錫めっき後クロメート処理を行っているために DI 加工そのものは可能であるが、金型の損傷が大きく、実用的でない。

実施例 1～実施例 5 は、本発明の要件をすべて満足しているので、DI 加工性は勿論、塗装後耐食性、外面缶底耐錆性等に優れた DI 缶用表面処理鋼板である。

Since Comparative Example 9 is performing the tin-plating back chromated treatment, the DI process itself is possible.

However, damage of a metallic mould is large and is not practical.

Since Example 1- Example 5 has satisfied all the requirements for this invention, DI workability is the surface-treated steel sheet for DI can excellent in of course, after coating corrosion resistance, the outside can-bottom rusting proof, etc.

[illegible]

(=) N に対する割合とは、 N に対する $N / (F_0 + N)$ が 0.03 (割合) 以上である N に対する割合をいう。

【発明の効果】

本発明は以上説明したように構成されているので、本発明方法により高価な錫の使用量を少なくした DI 缶用表面処理鋼板を提供できるようになり、しかも連続焼鈍、調質圧延、錫めっき等を連続的に同一ラインで行うため、製造コストを大幅に削減できるようになった。これらは

[EFFECT OF THE INVENTION]

Since this invention is composed as demonstrated above, it can provide the surface-treated steel sheet for DI can which decreased the amount of the expensive tin used by the method of this invention.

And since a continuous annealing, a temper rolling, the tin plating, etc. were continuously performed with the same line, the manufacturing cost could be reduced sharply.

It is anticipated that these demonstrate the effect that the cheap import can which has been

最近問題になっている安価な輸入缶に対抗できる効果を発揮するものと期待される。

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the problem recently can be opposed.

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